Research

Studies on Sulfur Diffusion into Cu(In,Ga)Se₂ Thin Films

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A systematic study was carried out to investigate the distribution of sulfur (S) in CuInSe₂ (CIS) and Cu(In,Ga)Se₂ (CIGS) absorbers which were exposed to an H₂S atmosphere at elevated temperature. Results demonstrated that S diffusion into CIS layers was a strong function of the original stoichiometry of the absorber before sulfurization. Sulfur inclusion into Cu-rich CIS films was much more favorable compared to S diffusion in Cu-poor layers. The sulfur distribution profile was also strongly influenced by the micro-structure of the original CIS and CIGS layers, with sections of the films with smaller grains accommodating more S. Copyright © 2000 John Wiley & Sons, Ltd.

INTRODUCTION

CuInSe₂ (CIS) is an important solar cell material with a bandgap value of about 1·0 eV. Addition of gallium (Ga) and/or sulfur (S) can tune the bandgap value of this chalcopyrite semiconductor in a continuous manner from 1·0 eV to about 2·4 eV, allowing the fabrication of high bandgap or graded bandgap device structures. The typical high efficiency CIS-based solar cell configuration is glass/Mo/absorber/CdS/ZnO. Having a large bandgap region near the surface of the absorber film where the junction is formed is desirable because this can potentially yield devices with high open circuit voltage (V_{oc}) values.

The highest efficiency polycrystalline thin film solar cell to date was fabricated on a graded Cu(In,Ga)Se₂ (CIGS) absorber deposited on a glass/Mo substrate by the evaporation method. This cell yielded an AM1·5 conversion efficiency of 18·8%.[1] Two-stage selenization processes have also been employed for the growth of absorbers that were used for the fabrication of over 15% efficient solar cells.[2,3] One such process involves H₂Se selenization of metallic precursors. In this technique, a metallic precursor film containing Cu, In and Ga is first deposited on the glass/Mo substrate. The precursor is then exposed to a H₂Se atmosphere at elevated temperatures, typically above 400°C, to form the CIGS compound. The Ga concentration in a CIGS absorber grown by this selenization approach is graded, with most of the Ga residing near the Mo/absorber interface. The Ga content near the surface region can be increased through a high temperature (> 525°C) heat treatment in an inert atmosphere facilitating Ga diffusion.[4,5]

A higher bandgap surface region can be formed on a CIGS absorber by sulfurization. Graded absorber structures with S-rich surface and Ga-rich contact regions have been grown and high efficiency solar cells have been fabricated on such graded absorbers.[2] Additional work describing S introduction into CIGS absorber layers by annealing these films in a H₂S atmosphere has also been published.[3,6,7] However, no systematic study of S distribution in films with varying composition and micro-structure has been carried

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Table I. The CIS and CIGS samples used in the sulfurization studies. Samples were grown by a two-stage selenization technique

Sample Number	Cu/In ratio	Cu/(In + Ga) ratio	Ga/(Ga + In) ratio
1973A	1·1		
1973B	0·98–1·0		
1973E	0·86		
1975A		0·95	0·1
1976A		0·95	0·25
1977A		0·95	0·4

out and no correlation has been established between the S distribution profiles and the Cu/(In + Ga) and Ga/(In + Ga) ratios in sulfurized CIGS layers.

The purpose of this work was a systematic investigation of S distribution in CIS and CIGS absorbers which were subjected to sulfurization in H_2S gas at an elevated temperature. The study was carried out on films with various Cu/In and Ga/(Ga + In) ratios to determine if changes in the original film composition would influence the resulting S concentration profile.

EXPERIMENTAL

In the previously published work related to CIGS film sulfurization, the CIGS layers were typically grown by the co-evaporation method at high temperatures. This process yields films with large grain size and high density. In the present study, CIS and CIGS films were grown by a two-stage selenization method. In this technique, Cu–In and Cu–In–Ga metallic precursors were first deposited on glass/Mo substrates by the e-beam evaporation technique and then selenized in a flowing 5% H_2Se + 95% N_2 atmosphere at around 450°C to form the selenides.[8] CIS films with Cu/In molar ratios varying from about 1·1 to 0·8 were obtained. Compositional variation was achieved by varying the thickness of the evaporated Cu, In and Ga layers. Film thicknesses were controlled using a crystal oscillator head mounted in the e-beam evaporation system. For the CIGS layers, the overall Cu/(Ga + In) ratio was fixed at 0·95 and the Ga/(Ga + In) ratio was varied by increasing the Ga content of the metallic precursor films. After selenization, the absorber layer thicknesses were measured by a TENCOR™ profilometer and were in the 2·0–2·5 μm range. The sample numbers and the information about the sample compositions are given in Table I.

The CIS and CIGS layers of Table I were subjected to a flowing 10% H_2S + 90% N_2 atmosphere at 575°C for 20 min for sulfurization. Auger depth profiles were obtained to determine S distribution in the sulfurized layers. It should be noted that Auger data provides the average S content which results from both grain boundary and bulk diffusion. Scanning electron micrographs (SEMs) were used to study the micro-structure of the absorbers.

RESULTS AND DISCUSSION

Figure 1 shows the S distribution profiles obtained from three different sulfurized samples using the Auger depth profiling technique. The rise in the Mo signal on the right indicates the approximate position of the Mo/CuIn(S,Se)$_2$ (CISS) interface for all three films. As can be seen from this data, there is a definite and strong relationship between the composition of the original CIS film and the distribution of S in the CuIn(Se,S)$_2$ absorber formed as a result of the sulfurization step. Sulfur distribution is near-uniform in the CISS film of Figure 1, which was obtained by the sulfurization of the Cu-rich CIS sample 1973A (Table I). Sulfur diffusion, on the other hand, was greatly curtailed in the near-stoichiometric sample,
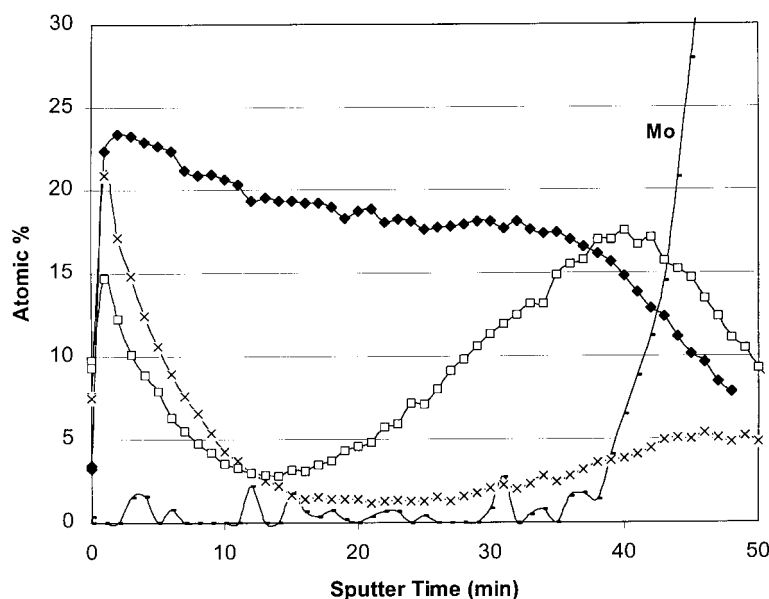
Figure 1. Auger depth profiles showing S distribution in the Cu-rich sample 1973A (◆), stoichiometric sample 1973B (X), and the In-rich sample 1973E (□) after these CIS films were sulfurized in an H_2S atmosphere at 575°C for 20 min

1973B, and the In-rich sample, 1973E. As shown in Figure 1, sulfurization of the near-stoichiometric CIS film gave a S profile with most of the S near the surface region. In this case there is little S deep in the bulk of the absorber. For the highly In-rich sample of 1973E, however, a large peak of S is observed near the Mo/absorber interface in addition to the S peak near the surface of the absorber. The (S + Se) distributions for all the samples of Figure 1 were plotted and found to be relatively flat, indicating that S has substituted for Se.

What could be the reason for the large differences observed between the S profiles of the three samples given in Figure 1? Sample 1973A before sulfurization was a Cu-rich CIS film with a Cu/In ratio of 1·1. Therefore, this film contained a secondary phase of Cu_2Se. Using the Cu/In ratio of 1·1, one can estimate that Se, which is chemically tied to the Cu_2Se secondary phase in this sample, constituted about 2·4 atomic percent of the total Se content. Therefore, an argument based on possible replacement of Se with S within the excess Cu_2Se phase during the sulfurization step could not explain the approximately 20 atomic percent S observed in the sulfurized layer. One possible explanation for the promotion of S inclusion in the Cu-rich CIS layer can be the existence of a liquid phase of Cu–(Se,S) in such films at the high sulfurization temperature of 575°C. It is plausible that kinetics of S inclusion is greatly accelerated by the presence of this phase which is expected to be on the film surface as well as in the grain boundary regions.

The micro-structure of CIS layers grown by the selenization technique is known to be strongly dependent on the Cu/In ratio.[9] Cu-rich layers typically have large columnar grains. Grain size in In-rich material, on the other hand, is smaller, especially near the film/Mo interface. The cross-sectional SEM of Figure 2(a) shows the micro-structure of sample 1973A after the sulfurization step. Grains that are larger than 2 μm in size can be seen in this Cu-rich material, which is well crystallized and dense. It should be noted that comparison of the cross-sectional SEMs of the absorber films before and after the sulfurization step indicated that the film micro-structure was formed and fixed during the selenization process and did not change further during the sulfurization treatment at 575°C.

There have been reports in the literature on the S distribution profiles in sulfurized CIGS layers. The Auger depth profile given in Tarrant and Ermer,[2] for example, showed high S concentration near the surface and contact region of an absorber layer which was used for the fabrication of a 15% efficient solar cell. However, the details of the processes employed for the growth of this absorber were not described.
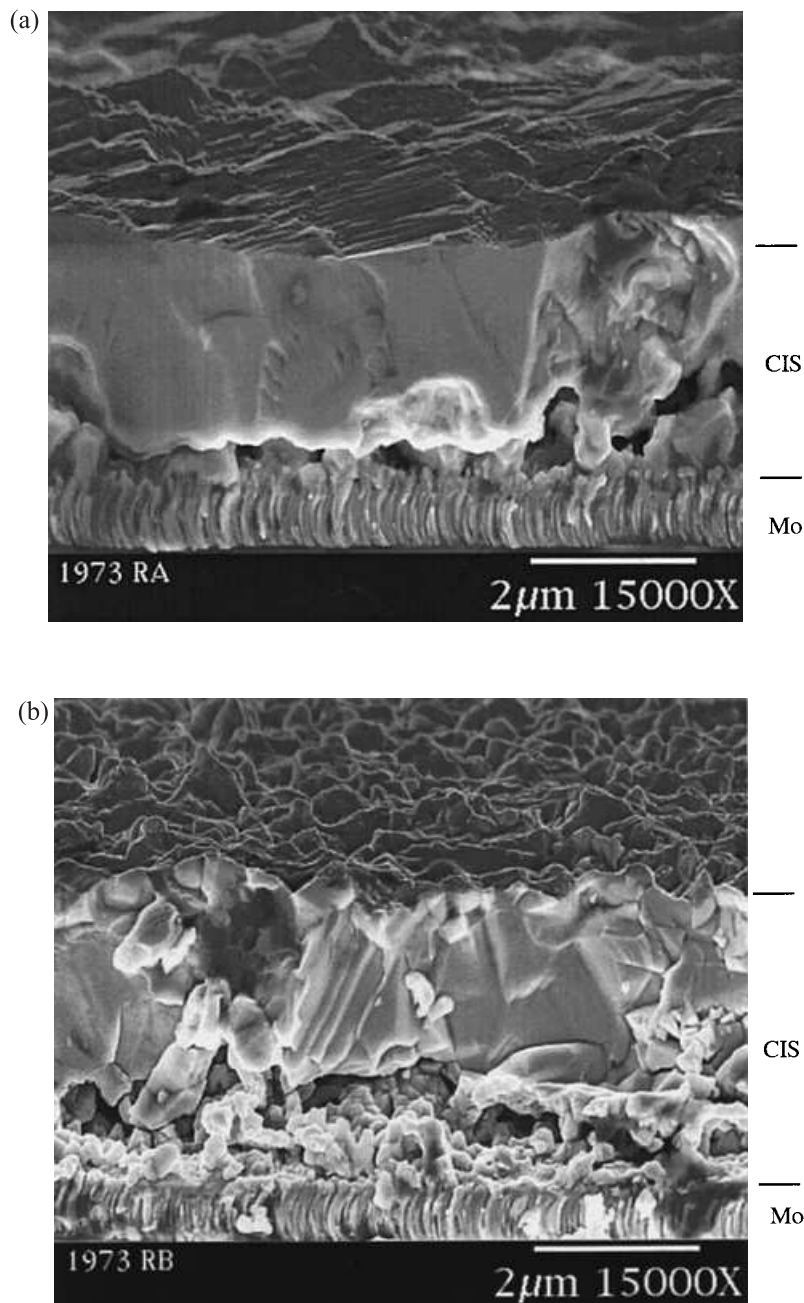
(a)

CIS

Mo

1973 RA   2 μm 15000X

(b)

CIS

Mo

1973 RB   2 μm 15000X

Figure 2. SEMS of cleaved samples (a) 1973A, (b) 1973B and (c) 1973E after the sulfurization step, taken at 80° tilt to show both the cross-section and the film surface. Samples 1973A, 1973B and 1973E had Cu/In ratios of about 1·1, 1·0 and 0·86, respectively

Nakada *et al.*,[6] upon their investigation of the sulfurization of co-evaporated CIGS layers, reported a S profile that was similar to the profile of sample 1973B of Figure 1. In that study the starting CIGS absorbers reportedly had large grain size and were near-stoichiometric, just as our sample 1973B.

The S distribution in the near-stoichiometric sample 1973B is an example of a diffusion profile with most of the S residing near the surface of the sulfurized absorber. However, the profile for the In-rich film
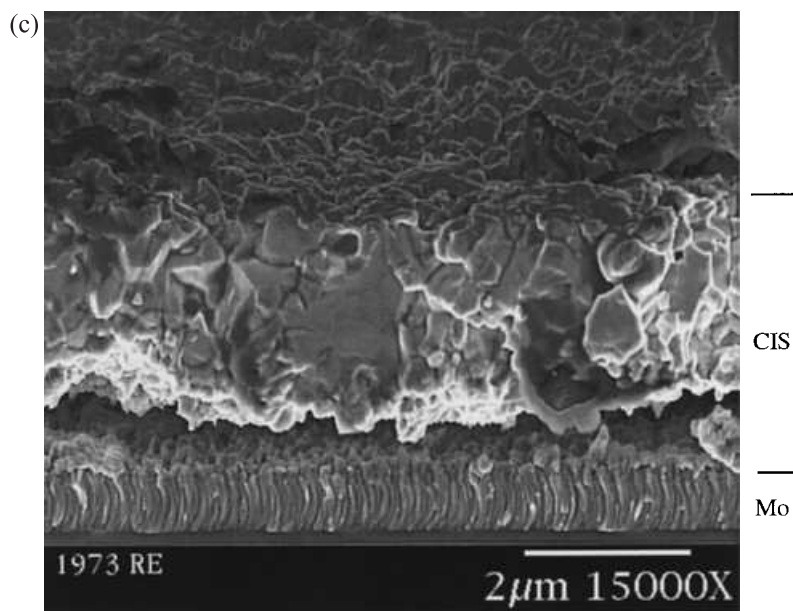
Figure 2. *Continued*

1973E has an additional S 'hump' near the Mo/absorber interface. This behavior can be explained by the micro-structural differences between the stoichiometric and the In-rich layers.

It is known that the grain size distribution through the thickness of a CIS film grown by the two-stage selenization technique is non-uniform, especially if the film is highly In-rich.[9] The typical micro-structure of such In-rich layers displays relatively large grains near the surface region and much smaller grains near the Mo/absorber interface. If S diffuses fast along the grain boundaries and then moves more slowly into the bulk of the grains, the small-grain region near the back contact of In-rich films is expected to accommodate more sulfur than the larger-grain bulk region. This, in turn, would give rise to the 'U-shaped' S profile as observed in Figure 1. The cross-sectional SEMs of the samples 1973B and 1973E shown in Figures 2(b,c) support this argument. The grains in sample 1973E are smaller than those in the well crystallized sample of 1973B, especially near the Mo contact. It should be noted that, although the SEMs of Figure 2 belong to sulfurized layers, they also represent the typical micro-structures of the original CIS absorbers, as stated earlier.

Nakada *et al*. had reported the effect of micro-structure on the S diffusion profile in sulfurized CIGS films.[6] In that study, the CIGS absorbers were grown by the co-evaporation method and the growth temperature was reduced from the standard 550°C to 370°C to obtain a uniformly small-grained film, which was then sulfurized. Sulfur content in the small-grained absorber was uniformly higher than that found in the standard large-grained film. In our In-rich samples with graded grain size, the S profile is also graded, giving rise to the observed double 'hump' behavior. It should be noted that this micro-structure-based argument may only be valid for the near-stoichiometric and In-rich absorbers. For the Cu-rich films, such as sample 1973A, the S diffusion mechanism must be drastically different because we would not expect to observe significant S diffusion into the large grain material of Figure 2(a) if the above micro-structure argument were singly invoked.

A model was recently offered to explain the mechanism of S diffusion into CIS layers by exposing the CIS surface to S vapors or H_2S gas.[10,11] According to this model, first a surface reaction, which is kinetically controlled, occurs between the CIS surface and the S source, forming a thin $CuInS_2$ layer. This is followed by an interdiffusion process between the $CuInS_2$ and the $CuInSe_2$ layers. Using this model, sulfurization data and XRD measurements on slightly Cu-rich CIS layers grown by the co-evaporation technique, Engelmann recently derived the bulk diffusion constant for S in CIS to be $D = 6 \times$

10^{-12} cm^2/s at 525°C.[11] The activation energy (Q) was also determined for the diffusion constant which followed an exponential dependence [$\propto \exp(-E/kT)$] on temperature. Using the value of D at 525°C and the thermal activation energy of 1·07 eV, we estimated the S bulk diffusion constant in slightly Cu-rich material to be about $1\cdot5 \times 10^{-11}$ cm^2/s at our sulfurization condition at 575°C. Considering the fact that $t = 20$ min anneal at this temperature would yield a $(Dt)^{1/2}$ value of about 1·34 μm, S would be expected to penetrate through most of the CIS absorber under our sulfurization condition, even without the contribution from the grain boundary diffusion. We have observed such a behavior only for the Cu-rich film of 1973A. The S profiles of the Cu-poor samples, on the other hand, suggested that the bulk diffusion constant of S in the near-stoichiometric or In-rich CIS layers should be much lower than the value previously reported in the literature. Taking the near-surface S profile of the near-stoichiometric sample in Figure 1, an estimate of the diffusion constant can be made. For a constant source of S at the surface of the film, the solution to the diffusion equation is the complementary error function.

$$C(x, t) = C_s \mathrm{erfc}(x/2(Dt)^{1/2}),$$

where $C(x, t)$ is the S concentration, C_s is the surface S concentration and x is the distance from the sample surface.[12] For the case of $x \ll 2(Dt)^{1/2}$, this equation can be simplified to.

$$C(x, t) = C_s(1 - x/(3\cdot14Dt)^{1/2})$$

and the value of D can be obtained from the slope of the $C(x,t)/C_s$ vs. x plot. Using $t = 1200$ s and x-values less than 0·09 μm, a diffusion constant of $D = 3 \times 10^{-13}$ cm^2/s was derived from the Auger data of Figure 1. The time axis of Figure 1 was converted into x for these calculations using the experimentally determined sputter etch rate of about 600 Å/min. Since $2(Dt)^{1/2}$ is in the order of 0·4 μm, the originally assumed condition of $x \ll 2(Dt)^{1/2}$ was found to be adequate for this estimation.

As can be seen from the preceding discussion, the diffusion constant value in Cu-poor material is about two orders of magnitude smaller than the value in Cu-rich material. Therefore, the S inclusion mechanism in CIS-type materials is a strong function of the original stoichiometry of the absorber. As stated before, the enhanced S distribution in Cu-rich CIS may be due to the existence of a Cu–(S,Se) phase. There is, however, also the possibility of the influence of intrinsic defects which are expected to be different in Cu-rich and In-rich CIS films. The exact nature of the S diffusion mechanisms in Cu-rich and In-rich CIS layers is currently under investigation. Time and temperature dependent studies of S profiles are being carried out to calculate the S diffusion constants in absorbers with various compositions.

It should be pointed out that the S in the sulfurized layers does not solely reside on the grain boundaries of the film, but it penetrates into the bulk of the grains. This has been confirmed by fabricating solar cells on In-rich CIS absorbers such as sample 1973E of Table I before and after the sulfurization step. The long wavelength cutoff of the quantum efficientcy (QE) data taken from these devices clearly showed bandgap widening in the sulfurized absorbers. The minimum bandgap value of the graded absorber derived from the QE measurement was in good agreement with the value expected from the Auger depth profiles. For example, sample 1973E after sulfurization has a region with 3 atomic percent S, corresponding to a bandgap value of about 1·03 eV compared to 1·0 eV for pure CIS.

The Auger depth profiles of CIGSS layers obtained by sulfurization of the Ga-containing CIGS films of Table I are shown in Figure 3. As expected, the Ga concentration is graded in these layers, with most of the Ga residing near the Mo/absorber interface.[5] Although the overall Cu/(Ga + In) ratio was fixed at the near-stoichiometric value of 0·95 for all three samples of Figure 3, the S concentration profile still displayed the double 'hump' behavior. The S content near the film surface stayed relatively constant, while the S peak near the Mo interface got larger as the overall Ga concentration increased. Once again, this preferred segregation of S into the Ga-rich regions of the absorber layers could be explained by the graded micro-structure within these films.

When the Cu/(In + Ga) ratio depth profiles were plotted for the three samples of Figure 3, it was observed that this stoichiometric ratio was in the range of 0·95–1·0 near the surface region, whereas it
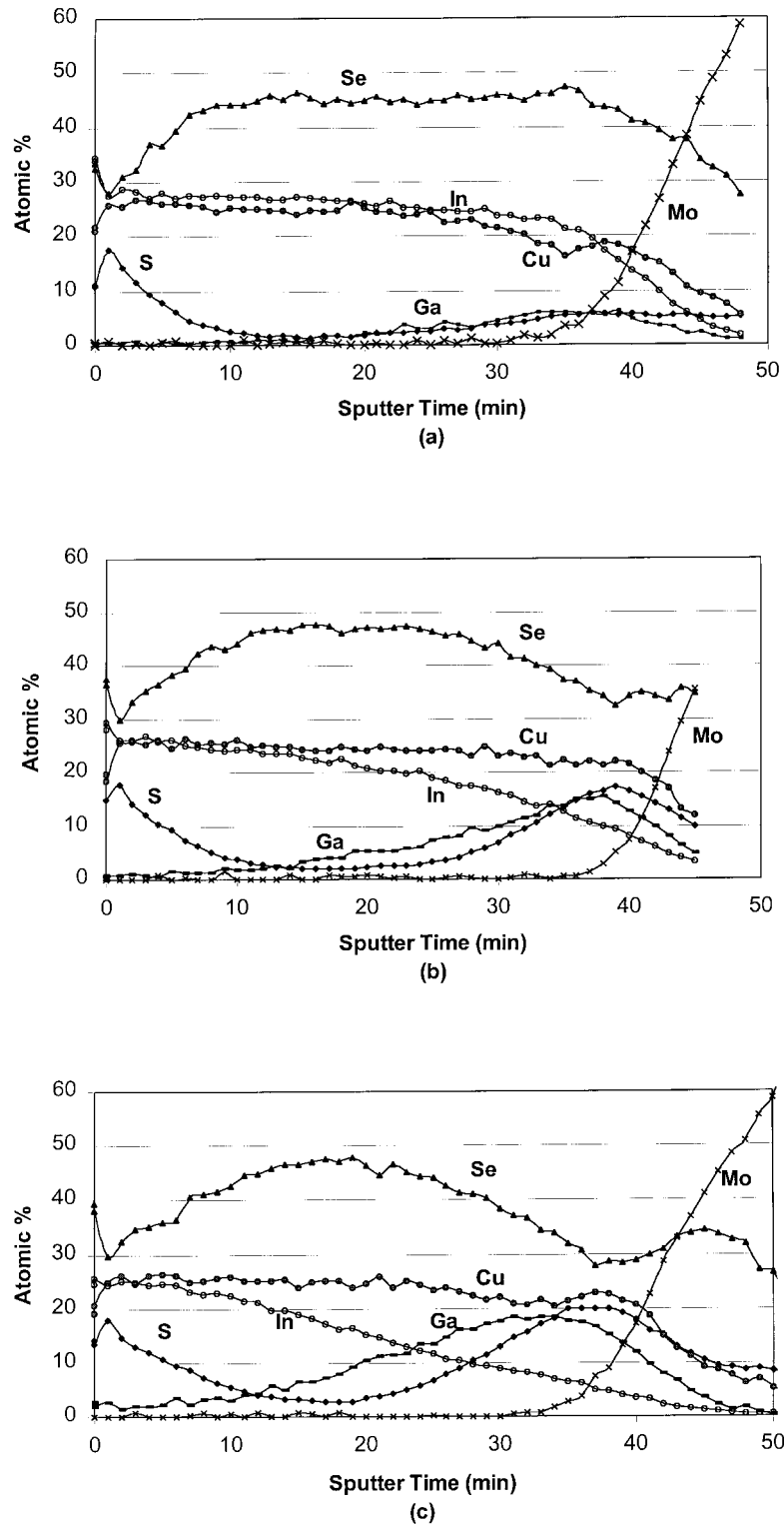
Figure 3. Auger depth profiles taken from samples (a) 1975A, with Ga/(Ga + In) = 0·1, (b) 1976A, with Ga/(Ga + In) = 0·25, and (c) 1977A, with Ga/(Ga + In) = 0·4, after these CIGS films were sulfurized in an H$_2$S atmosphere at 575°C for 20 min

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monotonically decreased to a value of 0·7–0·8 in the regions where Ga content peaked, i.e. both the Ga/(Ga + In) and the Cu/(In + Ga) ratios in these films were graded with regions near the Mo contact being both Ga-rich and Cu-poor. Furthermore, the Cu/(In + Ga) ratio near the Mo interface was the lowest for sample 1977A (Figure 3(c)) which contained the largest amount of Ga. Therefore, the small-grain region associated with the most In(Ga)-rich composition is expected to accommodate the highest concentration of S, as observed in the data of Figure 3(c). This micro-structural trend was observed and confirmed by the examination of the cross-sectional SEMs taken from the samples of Figure 3. It should be noted that, although both Ga and S happen to have concentration peaks near the Mo interface, we found no correlation between the Ga and S concentrations in these absorbers, i.e. S/Ga molar ratio was not a constant. Therefore, we can state that presence of S and Ga peaks in the same region of the samples was not due to a preferred chemical reaction between these two species.

CONCLUSIONS

The present study demonstrated that sulfurization of CIS and CIGS layers, which were grown by a two-stage selenization technique and then exposed to H_2S atmosphere, yielded S distribution profiles which were greatly influenced by the overall stoichiometry and the Ga content of the original selenide layers. It was found that the bulk diffusion constants of S in Cu-rich and Cu-poor CIS films were different by about two orders of magnitude, S inclusion being much more favorable in the Cu-rich material. The diffusion constant in Cu-poor material was estimated to be about 3×10^{-13} cm^2/s at 575°C. Observation of S peaks near the contact regions of Ga-containing graded absorbers and Cu-poor, Ga-free layers could be explained by the presence of small grained material near the Mo interface. These findings are important for the design of graded bandgap absorbers for high efficiency device fabrication.

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